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Interdiffusion of lateral composition modulated $(GaP)_2/(InP)_2$ short-period superlattices with different encapsulants

J. I. Malin,[a] A. C. Chen, J. E. Bonkowski, J. E. Baker, K. Y. Cheng, and K. C. Hsieh
Center for Compound Semiconductor Microelectronics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The interdiffusion of lateral composition modulated $(GaP)_2/(InP)_2$ short-period superlattices (SPSs) is reported. The lateral composition modulation is achieved by the strain induced lateral layer ordering (SILO) process. A blueshift in the interband transition is observed by photoluminescence spectroscopy for capless and SiO_2 encapsulated annealed SPSs (800 °C, 5.5 h), while the intensity and wavelength of Si_3N_4 encapsulated annealed SPSs are only slightly perturbed. From transmission electron microscopy, capless annealed SPSs (800 °C, 5.5 h) retain their lateral composition modulation, however, the $(00\frac{1}{2})$ satellite reflections disappear. For long anneal times (48 h), the interband transition corresponds to that of a $In_{0.50}Ga_{0.50}P$ alloy, suggesting the lateral composition modulation disappears. The observed lateral interdiffusion coefficient exceeds the vertical by a factor of ~30, suggesting SPS interdiffusion is enhanced by native point defects. [S0021-8979(96)07714-6]

Despite the exciting advances in the growth of lateral composition modulated structures,[1] only efforts to study vertical quantum well thermal stability have been undertaken.[2] The study is a necessary precursor for the investigation of post-growth annealed SPS devices such as impurity induced layer disordered (IILD)[3] and transverse junction stripe (TJS)[4] lasers. The technique of SPS interdiffusion is significant as a tool to better understand the as-grown lateral composition modulation which is prepared by the strain induced layer ordering (SILO) process.[1] Because interdiffusion depends on both the ambient (overpressure and encapsulant) and native point defect concentration,[5] various structural features may be inferred from the experiment.

The large density of states and spatial localization of electrons and holes associated with quantum confined lateral composition modulated structures (quantum wires) are predicted to yield low threshold lasing and increased modulation bandwidth. Although the best reported threshold for SILO-grown quantum wire lasers is 250 A/cm^2 at 77 K,[1] index-guided IILD quantum wire lasers are expected to achieve even lower thresholds as a 30% reduction in threshold is observed for IILD quantum well lasers.[3] Examination of active area (striped region) interdiffusion is first undertaken to determine the feasibility of IILD quantum wire lasers.

An undoped 100 pair (~1100 Å) lateral composition modulated $(GaP)_2/(InP)_2$ SPS is grown by gas-source molecular beam epitaxy (using the SILO technique) on a (001)-oriented undoped GaAs substrate. 1000 Å of SiO_2 or Si_3N_4 encapsulant is deposited by chemical vapor deposition at a temperature of 400 or 700 °C, respectively. Both the encapsulated sample and red phosphor (to maintain surface morphology) are evacuated ($\sim 10^{-6}$ Torr) in clean quartz ampoules and then annealed for various times and temperatures.

The interband transition of as-grown and annealed SPSs is characterized by 77 K photoluminescence (PL) spectroscopy using the linearly polarized 514.5 nm line of an Ar ion laser. Polarized PL (PPL) measurements are made by using an incident beam polarized parallel to the [110] direction with an analyzer oriented perpendicular and parallel to each of the incident beams. Cross-sectional transmission electron microscopy (TEM) identifies both interdiffusion and defect formation in annealed SPSs. The outdiffusion of Ga and In from the SPS into the dielectric encapsulant is measured by a Cameca IMS 5f ion microprobe (Cs+, 10 kV) secondary-ion-mass spectroscope (SIMS).

The interdiffusion mechanism is explored by evaluating the effect of phosphorous overpressure (P_4) on interband transition energy. In Fig. 1, an increase in the PL blueshift of capless annealed SPSs (850 °C, 5 h) is observed for increasing overpressures, suggesting interdiffusion is enhanced by column III vacancies, V_{III}, created at the surface.[6] Because the concentration of column III vacancies varies at the surface according to [5]

$$[V_{\mathrm{III}}] \propto P_{\mathrm{P4}}^{1/4},$$

interdiffusion is enhanced with increasing overpressure.[7] When the annealing time is increased from 5 h to 48 h, poor surface morphology is observed, indicating surface phosphorous depletion is time-dependent.

The role of vacancy enhanced interdiffusion is further explored on annealed capless and dielectric encapsulated (SiO_2 and Si_3N_4) SPSs. The PL spectrum of Fig. 2(b) reveals that the Si_3N_4 encapsulated annealed SPS (800 °C, 5.5 h, 0.2 atm) exhibits the least significant change in peak wavelength, intensity (to 3/5), and polarization (from 2.5 to 1.5). The SiO_2 encapsulated and capless annealed SPSs of Figs. 2(c) and 2(d), however, demonstrate a substantial blueshift and

[a]Present address: Code 5613, Naval Research Laboratory, Washington, DC 20375; Electronic mail:malin@tantalus.nrl.navy.mil

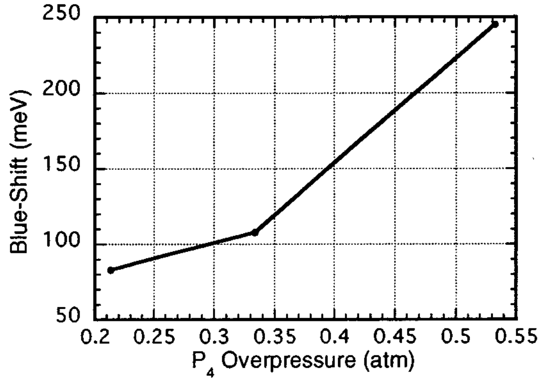

FIG. 1. Plot of energy blueshift vs P_4 overpressure for annealed SPSs (800 °C, 5 h). Increasing blueshift confirms vacancy enhanced interdiffusion.

reduction in both the intensity (to 2/5) and polarization (from 2.5 to 1). The more porous dielectrics (like SiO_2) permit more Ga to out-diffuse,[8] thereby creating vacancies which enhance SPS interdiffusion. For extended anneal times, however, SiO_2 saturates with column III atoms and suppresses interdiffusion.[9] An out-diffusion of both Ga and In ($\sim$200 Å) into the SiO_2 encapsulant is confirmed by SIMS for an annealed SPS (800 °C, 5.5 h).

The SILO-grown SPS structures are unique because the composition is modulated in both the [001] and [110] directions, and interdiffusion with respect to direction is treated differently. The lateral ([110]) interdiffusion of annealed SPSs is confirmed by minimized PL polarization.[1] The spectra of Figs. 2(c) and 2(d) exhibit blueshifts, demonstrating enhanced lateral interdiffusion for capless and SiO_2 encapsulated annealed SPSs. Additionally, the spectra of Figs. 2(c) and 2(d) no longer exhibit the fatigue peak (high energy shoulder). Either a change in fatigue lifetime or crystal composition is attributed to the capless and SiO_2 annealing.

The TEM of Fig. 3(a) shows that capless annealed SPSs (750 °C, 10 h) SPSs retain both the $(00\frac{1}{2})$ satellite reflections (demonstrated in the diffraction pattern inset) and lateral

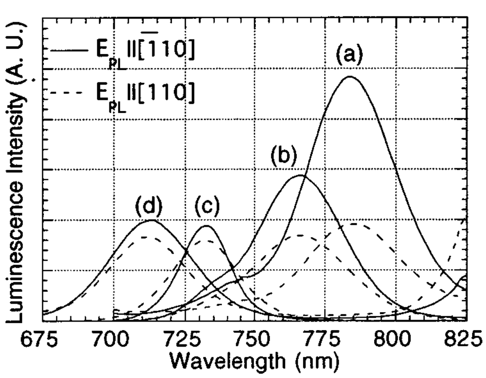

FIG. 2. PPL spectra of (a) as-grown SPS and (b) Si_3N_4, (c) capless, and (d) SiO_2 encapsulated annealed SPS (800 °C, 5.5 h). The minimal blueshift for Si_3N_4 suggests suppression of vacancy enhanced interdiffusion. For the capless and SiO_2 encapsulated annealed SPSs, large blueshifts and a reduced PL polarization is observed, suggesting interdiffusion of the lateral composition modulation.

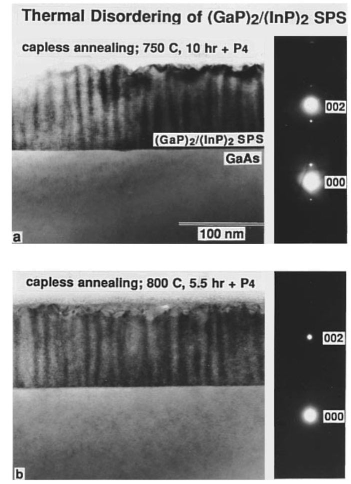

FIG. 3. TEM of capless annealed SPSs at (a) 750 °C for 10 h, and (b) 800 °C for 5.5 h. The $(00\frac{1}{2})$ satellite reflections and lateral composition modulation are preserved at 750 °C, however, for the 800 °C anneal, the satellite reflections no longer exist.

composition modulation. At a temperature of 800 °C, however, the $(00\frac{1}{2})$ satellite reflections corresponding to the vertical SPS disappear despite the preservation of the lateral composition modulation. For extended 800 °C anneals (48 h), the measured interband energy corresponds to $In_{0.50}Ga_{0.50}P$. Comparing the anneal time and vertical ($\sim$12 Å) and lateral ($\sim$200 Å) period dimensions, the calculated 800 °C lateral and vertical interdiffusion coefficients (according to $D\sim x^2/4t$) are 6×10^{-18} and 2×10^{-19} cm^2/s, respectively. Lateral interdiffusion enhancement is attributed to differing quantities of native point defects in the lateral composition modulated superlattice consisting of GaP and InP. This implies native point defects diffuse faster than surface generated vacancies.[5]

The increase in lateral SPS interdiffusion with overpressure, complemented by Si_3N_4 vacancy suppression confirm vacancy enhanced interdiffusion of $(GaP)_2/(InP)_2$ SPS. TEM and PL confirm the lateral interdiffusion coefficient, 6×10^{-18} cm^2/s, exceeds the vertical, 2×10^{-19} cm^2/s, by a factor of $\sim$30. This suggests the anisotropic formation of native point defects during growth which diffuse faster than surface generated vacancies. In addition to confirming the structural and interdiffusion characteristics of the SPS, this study demonstrates that Si_3N_4 masked IILD and TJS lasers will exhibit minimal degradation of active region quality for anneal temperatures as high as 800 °C. Achieving the appropriate impurity diffusion profile is the next step toward the realization of IILD and TJS lasers.

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